No-go theorem in many body dissipative particle dynamics

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Many body dissipative particle dynamics (MDPD) is a particle-based simulation method in which the interaction potential is a sum of self energies depending on locally-sampled density variables. This functional form gives rise to density-dependent pairwise forces, however not all such force laws are derivable from a potential and the integrability condition for this to be the case provides a strong constraint. A strategy to assess the implications of this constraint is illustrated here by the derivation of a useful no-go theorem for multicomponent MDPD.

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Dissipative particle dynamics (DPD) has attracted a lot of interest in its possibilities for modelling soft condensed matter [1, 2]. It is characterised by pairwise soft repulsive forces with a pairwise momentum-conserving thermostat [3]. Conceived somewhat later, many-body dissipative particle dynamics (MDPD) holds much promise as a second generation method [4–11], although it has mainly been applied to vapour-liquid coexistence and free surface simulations [7–11]. In the present note I explore the consequences for MDPD of allowing an arbitrary local density dependence into the pairwise repulsive forces. In particular if one requires that a potential exists, so that the forces are conservative, the allowed functional form of the pairwise forces is severely constrained. I will here outline a strategy for assessing the implications of this constraint, illustrated by the generation of a no-go theorem for a multicomponent MDPD force law that has been suggested in the literature [9, 10]. The present result also demonstrates that it is by far better to proceed from the potential to the forces, rather than the other way around.

Leaving aside the DPD thermostat, which has been well described elsewhere [12], standard DPD is characterised by pairwise repulsive forces of the form

$$\mathbf{F}_{ij} = A\, w_C(r_{ij})\, \hat{\mathbf{r}}_{ij} \tag{1}$$

where $\mathbf{F}_{ij}$ is the force acting between the ith and jth particles (at positions $\mathbf{r}_i$ and $\mathbf{r}_j$), A is a repulsion amplitude, $w_C(r)$ is a weight function, $r_{ij} = |\mathbf{r}_j - \mathbf{r}_i|$ is the spatial separation, and $\hat{\mathbf{r}}_{ij} = (\mathbf{r}_j - \mathbf{r}_i)/r_{ij}$ is a unit vector along the line of centres. I shall assume the weight function has compact support (*i. e.* $w_C = 0$ for $r > r_c$ where r_c is a cut-off distance) but for the present purposes it is not necessary to specify the exact functional form.

In contrast, MDPD starts from a rather different viewpoint. The potential energy in MDPD is a sum of density dependent one-body terms [4–8],

$$U(\{\mathbf{r}_i\}) = \textstyle\sum_i u(\overline{\rho}_i)\,, \tag{2}$$

where the one-body terms depend on local densities,

$$\overline{\rho}_i = \textstyle\sum_{i\neq j} w_\rho(r_{ij})\,. \tag{3}$$

From the potential one can derive the force law,

$$\mathbf{F}_i = -\frac{\partial U}{\partial \mathbf{r}_i} = \textstyle\sum_{i\neq j} \mathbf{F}_{ij}\,, \tag{4}$$

where

$$\mathbf{F}_{ij} = -[u'(\overline{\rho}_i) + u'(\overline{\rho}_j)]\, w'_\rho(r_{ij})\, \hat{\mathbf{r}}_{ij}\,. \tag{5}$$

Here $w_\rho(r) \geq 0$ is another weight function, also with compact support. Since the potential in Eq. (2) is a regular function of the particle positions, MDPD avoids issues that otherwise plague density-dependent pair interactions [13], although if the forces are not purely repulsive one should take care to ensure thermodynamic stability according to the criteria devised by Ruelle [14].

It is clear that the choice $u(\overline{\rho}) = A\overline{\rho}/2$ and $w'_\rho(r) = -w_C(r)$ brings Eq. (5) into agreement with Eq. (1). Hence standard DPD is just a special case of MDPD. Note that this may imply $\int d^3\mathbf{r}\, w_\rho(r) \neq 1$ but abandoning this normalisation requirement leads to a considerable notational simplification by eliminating unnecessary prefactors. Another example is $u(\overline{\rho}) = B\overline{\rho}^2/2$. Again setting $w_C = -w'_\rho$, this generates the force law

$$\mathbf{F}_{ij} = B\,(\overline{\rho}_i + \overline{\rho}_j)\, w_C(r_{ij})\, \hat{\mathbf{r}}_{ij}\,. \tag{6}$$

This force law (with $B > 0$) in combination with the standard DPD force law of Eq. (1) (with $A < 0$ and a larger cut-off) has been extensively used for free surface simulations. For a recent review see Ghoufi *et al.* [11]

Frequently DPD is applied to multicomponent systems and Eq. (1) is generalised to

$$\mathbf{F}_{ij} = A_{ij}\, w_C(r_{ij})\, \hat{\mathbf{r}}_{ij} \tag{7}$$

where A_{ij} is a matrix of repulsion amplitudes. It is natural to consider a similar generalisation of Eq. (6),

$$\mathbf{F}_{ij} = B_{ij}\,(\overline{\rho}_i + \overline{\rho}_j)\, w_C(r_{ij})\, \hat{\mathbf{r}}_{ij}\,. \tag{8}$$

This has been proposed in the published literature [9, 10], but my claim is that such a force law is *not* conservative

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unless B_{ij} is a constant matrix. This is the no-go theorem of the title. (In fairness to the authors of Refs. [9, 10], they actually only use the $B_{ij} = B$ case.)

How can the no-go theorem be proved? Hopefully it is obvious that a *sufficient* condition for a many body force law to be conservative is to display an explicit potential. For the present problem, if $B_{ij} = B$, such a potential is provided by Eqs. (2) and (3) with $u(\overline{\rho}) = B\overline{\rho}^2/2$ as already stated. A *necessary* condition for a force law to be conservative is that the 'Maxwell relation'

$$\frac{\partial \mathbf{F}_i}{\partial \mathbf{r}_j} = \frac{\partial \mathbf{F}_j}{\partial \mathbf{r}_i} \tag{9}$$

is satisfied. This follows from the first part of Eq. (4). The application of this to a general configuration of N particles is not straightforward since both sides of Eq. (9) contain multiple sums. However Eq. (9) should hold for *any* configuration of particles, so we can choose a configuration at our convenience. For the present problem therefore, let us select one which contains an isolated collinear triplet of particles. Without loss of generality we can place the particles on the x-axis at positions $x_1 < x_2 < x_3$. I shall define $x_{ij} = x_j - x_i$. We can further suppose $x_{13} < r_c$ so that all particles interact. The pairwise forces are (setting $w_C = -w'_\rho$)

$$\begin{aligned} F_{12} &= -F_{21} = -B_{12}\,(\overline{\rho}_1 + \overline{\rho}_2)\,w'_\rho(x_{12})\,, \\ F_{13} &= -F_{31} = -B_{13}\,(\overline{\rho}_1 + \overline{\rho}_3)\,w'_\rho(x_{13})\,, \\ F_{23} &= -F_{32} = -B_{23}\,(\overline{\rho}_2 + \overline{\rho}_3)\,w'_\rho(x_{23})\,. \end{aligned} \tag{10}$$

The local densities are $\overline{\rho}_1 = w_\rho(x_{12}) + w_\rho(x_{13})$, $\overline{\rho}_2 = w_\rho(x_{12}) + w_\rho(x_{23})$, $\overline{\rho}_3 = w_\rho(x_{13}) + w_\rho(x_{23})$; and the total forces are $F_1 = F_{12} + F_{13}$, $F_2 = F_{21} + F_{23}$, $F_3 = F_{31} + F_{32}$. Let us define $D_{ij} = \partial F_i/\partial x_j - \partial F_j/\partial x_i$. By explicit calculation I find $D_{12} = D_{23} = D_{31}$ where

$$\begin{aligned} D_{12} = {} & (B_{13} - B_{23})\,w'_\rho(x_{13})\,w'_\rho(x_{23}) \\ & + (B_{12} - B_{13})\,w'_\rho(x_{12})\,w'_\rho(x_{13}) \\ & + (B_{12} - B_{23})\,w'_\rho(x_{12})\,w'_\rho(x_{23})\,. \end{aligned} \tag{11}$$

Thus we see the D_{ij} vanish if and only if $B_{12} = B_{13} = B_{23}$, since by choice all the $w'_\rho(x_{ij})$ factors are strictly negative. Moreover we can pick *any* three particles for this argument. Hence the Maxwell relation fails in at least in a *subset* of configurations, unless B_{ij} is a constant matrix. This completes the desired proof of necessity.

An analogous argument does not go through for Eq. (7) since in that case we can exhibit an actual potential, namely $U = \sum_{i>j} A_{ij} w_\rho(r_{ij})$, although this does not reduce to a sum of self energies unless $A_{ij} = A_i + A_j$. Of course one can additively combine force laws, so it is possible to have conservative multicomponent MDPD based on Eqs. (6) and (7). Other approaches have been described by Trofimov *et al.* [5] and Merabia *et al.* [8].

Why is it so important that the force law be conservative? The answer is that for many applications one wishes to use the machinery of equilibrium statistical mechanics and thermodynamics [15], which requires the existence of a potential so that the steady state is given by Gibbs-Boltzmann. Of course the absence of a potential does not preclude the existence of a *non*-equilibrium steady state. Hence the effects of a non-conservative force law could be quite subtle, a bit like a failure to satisfy detailed balance in a Monte-Carlo simulation [1].

Here the general strategy to prove the no-go theorem has been to identify a convenient particle configuration for which the sums implicit in Eq. (9) become manageable. Presumably this could be applied in other cases too, but it would seem that at least $N \geq 3$ particles are required since a central force between a pair of particles can always be integrated to a pair potential. The converse implication is that a similarly defined potential for assembling $N \geq 3$ particles would depend on the assembly path, unless Eq. (9) holds.

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